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**NUCLEOPHILICITIES OF PULPING REAGENTS (II):
REACTIONS WITH A SATURATED CARBON CENTER**

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a Saturated Carbon Center

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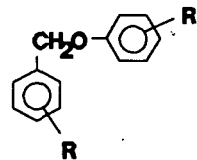
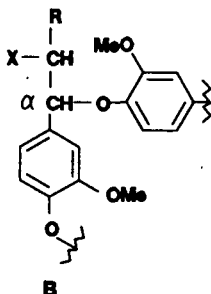
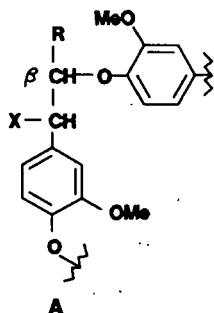
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ABSTRACT

The reaction of 3-[3'-(α,α,α -trifluoromethyl)phenoxy]methyl]benzoic acid with selected ions was studied to determine relative nucleophilicities at 195°C in water. Nucleophilic displacement by the ions occurred at the benzyl carbon to liberate a phenolic group. The primary products of the displacement were independently synthesized and reacted in alkali to determine their stability. Hydrosulfide ion was 20 times more reactive than hydroxide ion with this substrate, while anthrahydroquinone ion was 17 times more reactive.

INTRODUCTION

Wood is principally composed of fibrous carbohydrate material and amorphous polymeric lignin. The goal of chemical pulping is to remove the lignin component while retaining the carbohydrate fibers. Lignin monomer units are held together largely by alkylaryl ether bonds, with the β -O-4 type (A) accounting for 50-60% of the intermolecular linkages and the α -O-4 type (B) for 6-8%.¹ The role of pulping promoters is to assist in cleaving these ether bonds, which often leads directly to alkali-soluble phenolic products.



- 1, R = H, R' = p-COOH
2, R = p-COOH, R' = p-NO₂
3, R = m-COOH, R' = m-CF₃

One way pulping reagents can promote delignification is by functioning as nucleophiles.² The effectiveness of pulping reagents may be related to their relative nucleophilicities in water at 170°C, the conditions of pulping. This report addresses the relative nucleophilicities of selected ions at high temperatures in aqueous alkali toward an alkylaryl ether substrate (a saturated

carbon site). A corresponding study involves the relative nucleophilicities of pulping ions toward a conjugated unsaturated carbon site.³ Attack of reagents at both types of sites could be important to effective delignification.

Nucleophilicity not only depends on the type of substrate under attack, but many other factors, including solvent type and reaction temperature.⁴ It is not clear how effectively nucleophiles will be solvated at 170–200°C and whether the nucleophilic orders observed at room temperature will apply at high temperatures. A fundamental understanding of these issues is important to developing better pulping systems.

RESULTS AND DISCUSSION

Substrate Selection

A model compound was needed which exhibited good reactivity at 170°C, would not undergo competing base-promoted elimination reactions, and represented the abundant ether linkages present in lignin. The alkali-soluble benzyl aryl ether compound 1 was the first model selected for study. It was anticipated that the benzyl ether would be more reactive than an alkyl aryl ether toward S_N2 reactions⁴ and provide more latitude for reaction temperature variation. However, compound 1 was found to be relatively stable at 170°C in aqueous alkali.

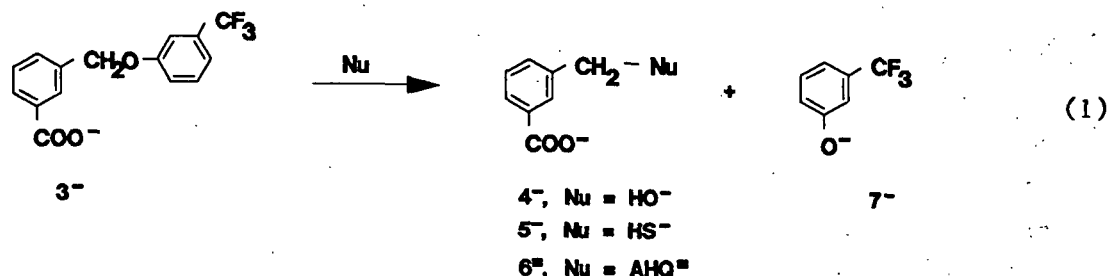
Compound 2, which contains a nitro group on the phenolate portion of the molecule, was sufficiently reactive in sodium hydroxide solutions at 170°C. The electron-withdrawing group enhances the reactivity of site under attack and provides additional stabilization of the negative charge on the leaving phenolate ion. The nitro group, however, was not stable to hydrosulfide ion at 170°C. Compound 2, therefore, was not a suitable model compound.

Structure-reactivity studies indicate that the trifluoromethyl group is a relatively strong electron-withdrawing group, though not as strong as the nitro group.⁴ Therefore, benzyl ether 3 was synthesized and studied. The trifluoromethyl group was placed at the meta position in compound 3 to avoid undesirable steric effects of an ortho position and possible quinonemethide formation at the para position. Quinonemethide formation of the liberated phenolate ion would hamper product analysis.

Mechanistic Studies

The reactions of compound 3 were investigated in oxygen-free water

solutions which contained hydroxide, hydrosulfide, and anthrahydroquinone ions. The expected reaction pathway of 3 is shown in Eq. 1. The disappearance of 3 and formation of products was followed using GC techniques. The identities of all products were confirmed by synthesizing or purchasing the products and comparing their GC and GC-MS properties.



Compound 3 was heated in aqueous sodium hydroxide, simulating soda pulping reactions, to give 3-(α -hydroxymethyl)benzoic acid (4) and 3-(α,α,α -trifluoromethyl) phenol (7) (Eq. 1, $\text{Nu} = \text{HO}^-$). Analysis of the reaction products, shown in Fig. 1, indicated roughly a 100% mass balance when adding the concentrations of the starting material of 3 and product 4; less than a perfect balance existed when adding the concentrations of 3 and product 7.

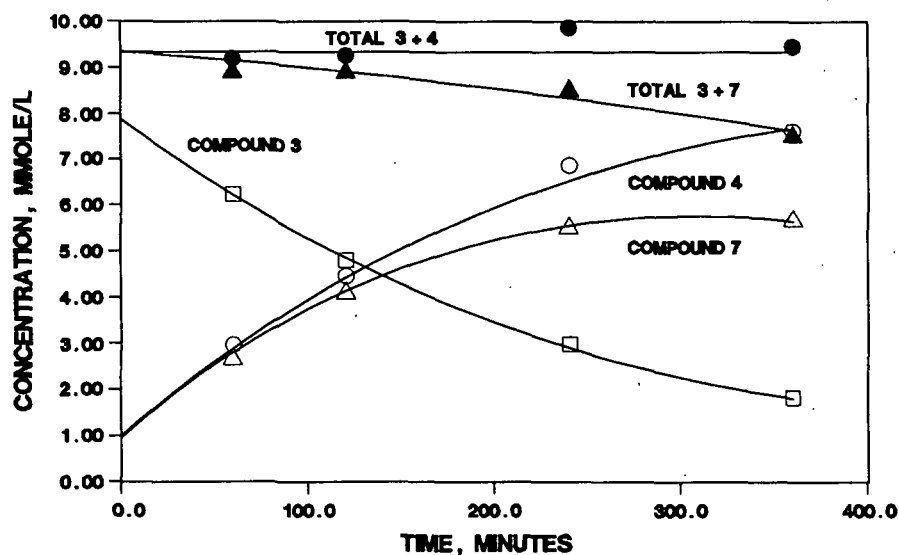


Figure 1. Mass balance for the reaction of 3 in 1.04 M NaOH at 195°C.

The stabilities of products 4 and 7 were investigated. The benzyl alcohol 4 did not react with hydroxide ion to form secondary products. The product

phenol 7, however, degraded after extended reaction times. Its concentration decreased by approximately 40% over a six hour period at 195°C. The rate of disappearance of 7 was not increased by the presence of hydrosulfide ion. Products from the reaction of 7 were not found by GC-MS. Resorcinol, a possible product of hydroxide substitution at the site of the trifluoromethyl group on 7, was not observed. Resorcinol was also found to degrade under similar conditions except at a slower rate.

Reactions similar to those which caused the degradation of 7 did not appear to consume the starting material 3. The mass balance between 3 and the product 4 was constant while that between 3 and the product phenol 7 was not constant at extended reaction times. This indicated that only 7 was unstable.

Compound 3 was heated in solutions containing sodium sulfide; the latter should be completely hydrolyzed to hydroxide and hydrosulfide ions.⁵ Conditions were chosen to simulate kraft pulping reactions. The primary products of the reaction were expected to be 3-(α -mercaptomethyl)benzoic acid (5), from HS^- displacement, and 3-(α -hydroxymethyl) benzoic acid (4), from HO^- displacement, and the phenol 7 (eq. 1, $\text{Nu}^- = \text{HO}^-$ and HS^-). Analysis of the reaction mixture showed a good mass balance between 3 and 7 (Fig. 2).

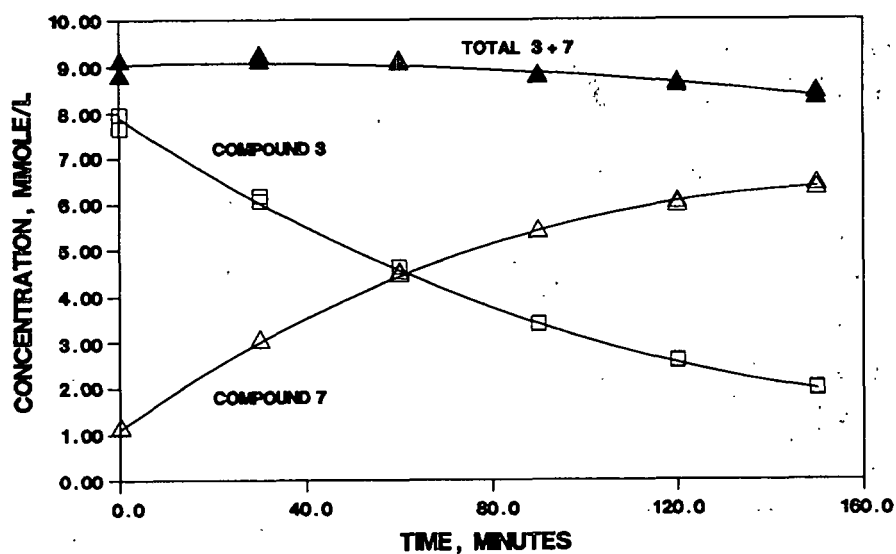
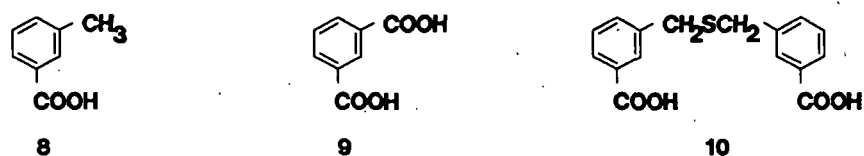


Figure 2. Mass balance for the reaction of 3 in 0.958 M NaOH and 0.0874 M NaSH at 195°C.

The relative amounts of products 4 and 5 formed will reflect the relative nucleophilicities of HO^- and HS^- . For example, if the two ions have identical

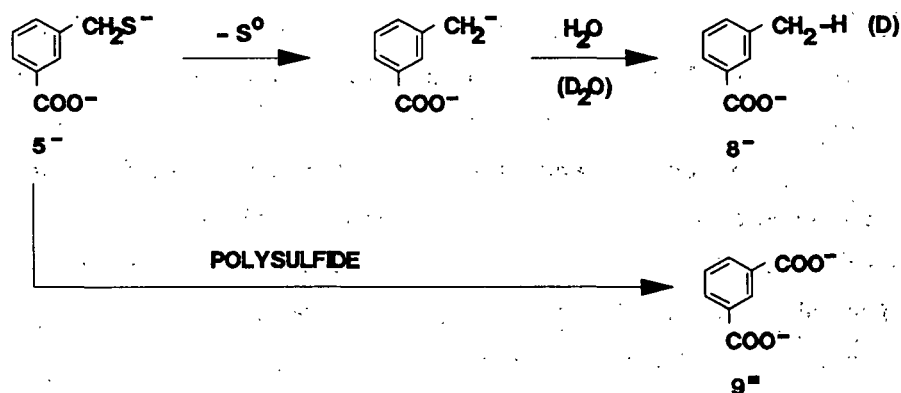
nucleophilicities, the ratio of 4:5 should be 11:1 based on the 11:1 ratio of HO^- to HS^- employed. The benzyl alcohol 4, already shown to be stable in 195°C -alkali, was observed in only trace amounts. The benzyl mercaptan 5 was not detected, but secondary products derived from 5 were observed. Based on product analyses, HS^- appears to be superior to HO^- as a nucleophile in displacement reactions of 3 at 195°C .

The hydrosulfide reaction gave rise to three new products, 3-toluic acid (8), isophthalic acid (9), and 3-(3'-carboxybenzyl-thiomethyl)benzoic acid (10), which were suspected to be secondary reaction products of mercaptan 5. An independently synthesized sample of compound 5 was degraded at a moderate rate in 195°C to form primarily 8 with small amounts of 9.



When either starting material 3 and intermediate 5 were heated in a deuterium oxide solution containing sodium deuterioxide, the toluic acid formed had one deuterium atom incorporated into its methyl group. This evidence supports the conclusion that toluic acid (8) is formed from 5 by loss of elemental sulfur and protonation of the resulting carbanion (Scheme 1). In the presence of hydrosulfide ions or elemental sulfur, however, compound 5 was very rapidly converted to 9, with lesser amounts of 8. Polysulfide, formed from elemental sulfur, may act as an oxidant to form 9 (Scheme 1).

SCHEME 1



Mercaptan 5 was also reacted with starting material 3 at 195°C. Analysis of the product mixture showed formation of 8 and 9, as well as 3-(3'-carboxybenzylthiomethyl)benzoic acid (10); the latter apparently is formed by the nucleophilic attack of 5 on the starting material. Compound 10 was shown to be stable in solutions containing hydroxide and hydrosulfide ions. In addition, the degradation rate of starting material 3 was virtually unaffected by the presence of the dimer (Fig. 3). Compound 10, therefore, was considered to be a stable end product.

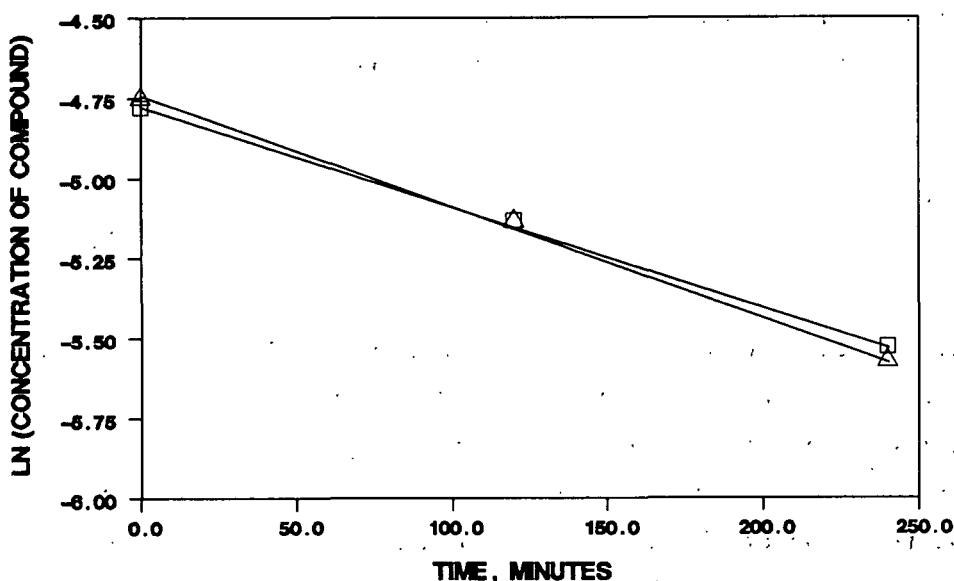


Figure 3. Comparison of the reaction rates of 3 (9.0 mM) in 1.05 M at 195°C in the presence, Δ , and absence, \square , of 9.0 mM of compound 10.

Compound 3 was heated in solutions containing both hydroxide and anthrahydroquinone ions to simulate soda-AQ pulping reactions. The expected primary products were compound 4, 10-hydroxy-10-(3'-carboxybenzyl)-9(10H)-anthracenone (6), and 3-(α,α,α -trifluoromethyl)phenol (7) (Eq. 1, $\text{Nu}^- = \text{HO}^-$ and AHQ^{2-}). Analysis of the reaction mixture showed a good mass balance between 3 and 7 (Fig. 4). Once again, only trace amounts of 4 were detected, indicating anthrahydroquinone ion was a much stronger nucleophile than hydroxide ion. Compound 6 was also observed in only trace amounts. Instead, a number of secondary products, including 8 and 9, were detected. Moderate amounts of compounds 11, 12, 13 were also identified by GC-MS.

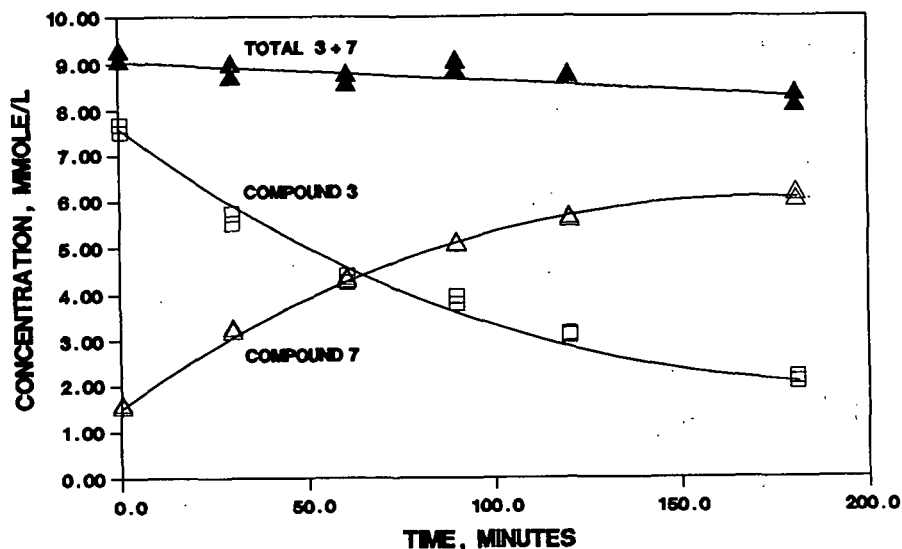
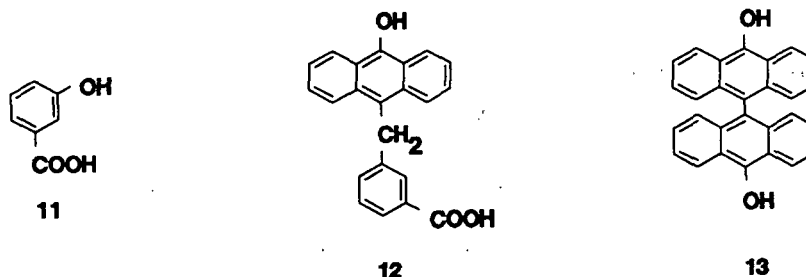


Figure 4. Mass balance for the reaction of 3 in 0.785 M NaOH and 0.0872 M AHQ at 195°C.



The reactions of the compound 6 were investigated to determine its degradation pathways. An independently synthesized sample of 6 was found to degrade to primarily 8 and 9 in soda and soda-AHQ reactions. Minor components of the reaction mixture included compounds 11, 12, and 13. Compound 13 was also formed under reaction conditions in AHQ solutions which did not contain model compounds or their degradation products. Based on these findings, it was concluded that anthrahydroquinone reacted with compound 3 to form primary product 6, and that this product decomposed to form the various secondary products shown above.

Kinetic Studies

Compound 3 was heated at 195°C in oxygen-free aqueous solutions which contained hydroxide, and combinations of hydroxide with hydrosulfide, anthrahydroquinone, sulfite (SO_3^{2-}), and thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ions. Excesses of each reagent were used so that their concentrations remained essentially constant;

the excellent fit of the data over two half-lives verified that the reactions followed pseudo-first order kinetics (Fig. 5).⁶ Because changes in the ionic strength of the medium could alter the observed rate constants, the ionic strength was generally maintained near 1.05 M.

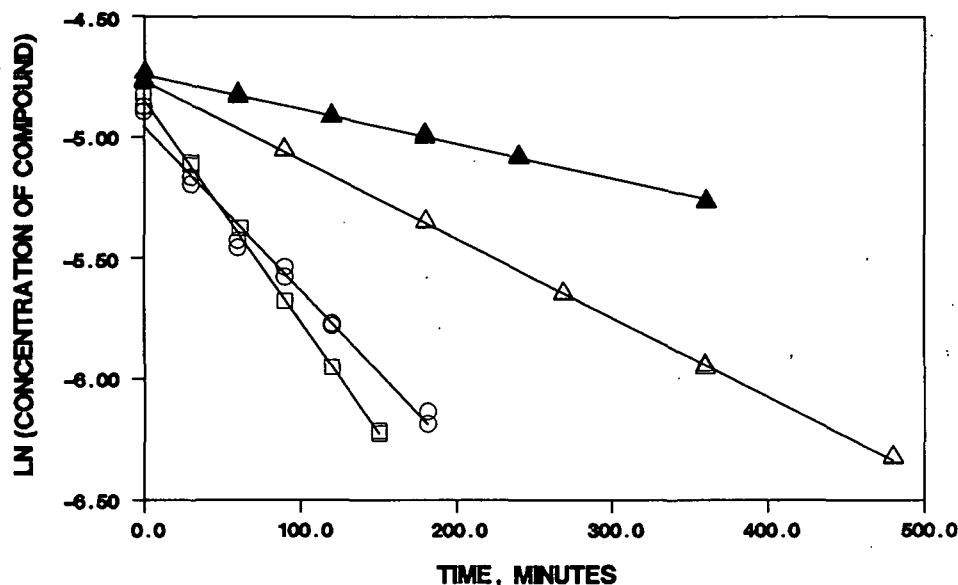


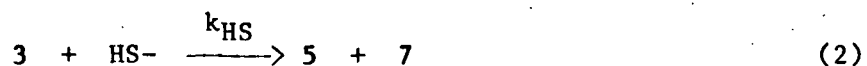
Figure 5. Pseudo-first order reactions of 0.0090 M compound 3 at 195°C: Δ, 1.05 M NaOH; ▲, 0.519 M NaOH; □, 0.958 M NaOH and 0.0874 M NaSH; ○, 0.785 M NaOH and 0.0872 M AHQ.

The slopes of the lines (Fig. 5) were calculated from regression analysis to obtain the observed rate constants, from which specific rate constants were calculated;³ correlation factors (R^2) were 0.996 or better for NaOH and NaOH/NaSH reactions and 0.985 for NaOH/AHQ. Triplicate runs were generally performed, with the exceptions being Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_3$ where a single run, with a limited number of data points, were obtained. Only crude estimates of nucleophilic strengths were needed in the latter cases.

The reactions between 3 and the various ions were assumed to be first order with respect to the nucleophile. A reaction order of 1.1 for hydroxide ion was calculated for observed rate constant observed for sodium hydroxide concentrations 1.05 M and 0.519 M (Fig. 5).

Compound 3 appeared to react with hydrosulfide ion to form an unstable mercaptan (5). In a subsequent reaction, the product 5 may react with the starting material to form a secondary product, dimer 10. This reaction consumes starting

material and, thus, would inflate the calculated rate constant of $125 (\pm 5) \times 10^{-5} \text{ sec}^{-1}$ for hydrosulfide ion. The various reactions occurring were assumed to be those listed in Eq. 1-5. Rate expressions, shown in Eq. 6-8, were derived to determine the true rate constant for hydrosulfide ion. In Eq. 7, $d[5]/dt$ is approximately zero using a steady state approximation.⁶



$$d[3]/dt = -k_{\text{HO}} [3] [\text{HO}^-] - k_{\text{HS}} [3] [\text{HS}^-] - k_{\text{Dimer}} [3] [5] \quad (6)$$

$$d[5]/dt = k_{\text{HS}} [3] [\text{HS}^-] - k_{\text{Dimer}} [3] [5] - k_8 [5] - k_9 [5] \approx 0 \quad (7)$$

$$d[10]/dt = k_{\text{Dimer}} [3] [5] \quad (8)$$

The concentration-time data for 3 and dimer 10 (Fig. 6) were fit in quadratic equations (r^2 values of 0.999 and 0.991, respectively) and derivatized to determine $d[3]/dt$ and $d[10]/dt$ at various times throughout the degradation. Substitution of Eq. 8 into Eq. 6 resulted in determination of k_{HS} of $106 \times 10^{-5} \text{ sec}^{-1}$. No confidence intervals were assigned, since the error analysis produced large values due to its dependence on time; a 95% confidence interval of $\pm 5-10 \times 10^{-5}$ would be expected since the rate constant was reduced by only 15%.

The sodium sulfide solutions employed in these studies contained 6% sodium sulfite and 2% sodium thiosulfate as impurities. The effect of these sulfoxy species on the degradation of 3 was also investigated. Starting material 3 (9.0 mmoles/6) was heated in one solution containing 0.869 M sodium hydroxide and 0.0881 M sodium sulfite and in a second solution containing 0.869 M sodium hydroxide and 0.0890 M sodium thiosulfate. Analysis of the data showed both sulfite and thiosulfate ions were more reactive than hydroxide ion, with rate

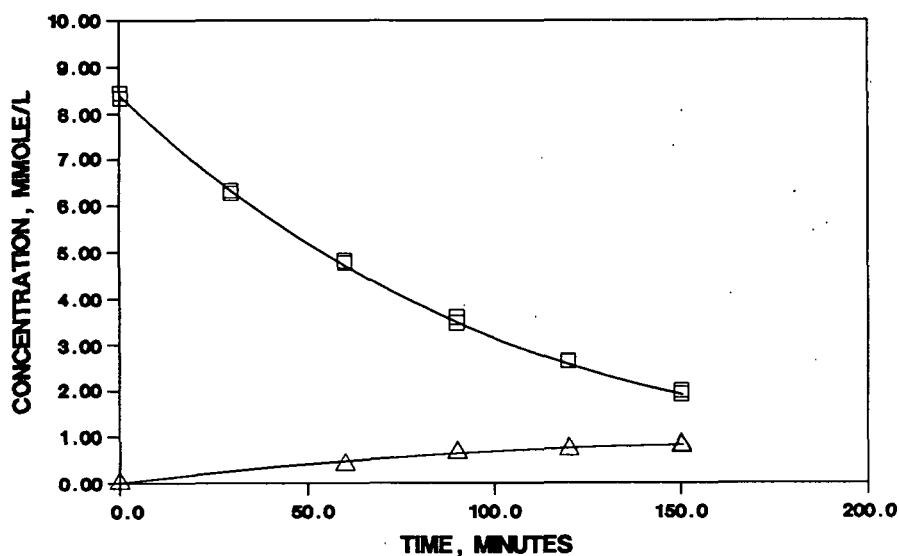


Figure 6. Concentration vs time profiles for the disappearance of compound 3, \square , and appearance of dimer 10, Δ , for the reaction of 3 with NaSH/NaOH at 195°C.

constants of $43 (\pm 12)$ and $47 (\pm 23) \times 10^{-5} \text{ sec}^{-1}$, respectively. The large 95% confidence interval reflects the fact that (a) duplicates were not performed, (b) only three time periods (including the zero time) were used to calculate the rate constant, and (c) the experimental error associated with the hydroxide ion rate constant is propagated through the calculations.

Rate constants of the reaction of 3 with the various nucleophiles studied are shown in Table 1. The experimental errors for the various nucleophiles are larger than that for hydroxide, since hydroxide ion is present during the other nucleophile reactions and the error limits associated with hydroxide ion are propagated through the calculations. Although precautions were taken to eliminate oxygen during the experimental setup, low levels of oxygen could affect AHQ^{-2} and HS^{-} concentrations and help contribute to the larger 95% confidence limits in these cases.

CONCLUSIONS

Hydrosulfide and anthrahydroquinone ions were much more reactive than hydroxide ion at 195°C toward the saturated carbon center in 3-[3'-(α,α,α -trifluoromethyl)phoxymethyl]benzoic acid. This conclusion is based on relative rate constants (Table 1) and the very low levels of hydroxide displacement

TABLE 1

Reaction Rate Constants of 3 at 195°C.

Nucleophile	$10^5 k, \text{ sec}^{-1} (\pm 95\% \text{ CI})^a$	k_{rel}
NaOH	5.2 ± 0.1^b	1
NaSH	$103 \pm (5-10)^{b,c}$	20
Na ₂ AHQ	9.9 ± 8.5^b	17
Na ₂ SO ₃	43 ± 12^d	8
Na ₂ S ₂ O ₃	47 ± 23^d	9

- a) CI signifies the confidence interval; see text for discussion of error estimate.
- b) Average of triplicate kinetic determinations, each involving duplicates at six time periods.
- c) The average rate constant was calculated by subtracting the contributions of 6% sodium sulfite and 2% sodium thiosulfate which were present in the sodium sulfide solution.
- d) Based on very limited data; see text for discussion.

product 4 observed in competitive experiments where the level of NaOH was much greater than that of the other nucleophiles. The enhanced reactivity of hydrosulfide ion with the saturated carbon center, compared to hydroxide ion, suggests that significant solvation is still present at pulping temperatures.

The relative nucleophilicities of these pulping ions was somewhat different for addition reactions to an unsaturated carbon site at 195°C; the order observed was $\text{AHQ}^{-2} > \text{HO}^- \approx \text{HS}^3$. Knowledge of the nucleophilicity of these species toward both saturated and unsaturated carbon centers has implication toward understanding the important steps during pulping. An HX^- nucleophile can add to an unsaturated site in lignin and, upon deprotonation, act as an internal nucleophile. Neighboring group mechanisms (intramolecular $\text{S}_{\text{N}}2$ reactions at saturated ether carbon atoms) are known to contribute to lignin fragmentation.¹ The nucleophilicities of alcohols and mercaptans (substituted nucleophiles) toward saturated carbon centers are known to parallel those of hydroxide and hydrosulfide ions at room temperature.⁴

The efficiency of the kraft pulping process appears to be related to the high nucleophilicities of hydrosulfide ion and lignin-attached mercaptide groups which can promote direct and neighboring group displacements at aryl ether bonds. The high efficiency of anthraquinone pulping processes appears to be related to the high nucleophilicity of AHQ^{-2} , efficient internal fragmentation

processes, and/or the existence of low energy, electron transfer fragmentation processes.⁷ Both sodium sulfite and sodium thiosulfate appear to be good nucleophiles in reactions at either a saturated or unsaturated³ carbon. Thiosulfate is present during kraft pulping and may assist in the delignification process. Pulping with sulfite has been a commercially viable process for several decades; the apparent good nucleophilic properties of the sulfite ion at high temperatures obviously contribute to its effectiveness in promoting delignification.

EXPERIMENTAL METHODS

Specific instrumentation employed has been previously described.³

3-[3'-(α,α,α -Trifluoromethyl)phenoxy]methyl]benzoic Acid (3). The following procedure was modified from Haslam and co-workers who synthesized similar compounds.⁸ Methyl α -bromo-3-toluate⁹ (10.0 g, 43.6 mmol) and potassium carbonate (6.7 g, 48.3 mmol) were dissolved in acetophenone (50 mL). The solution was heated to 150°C with stirring. A solution of 3-(α,α,α -trifluoromethyl)-phenol (7.8 g, 48.4 mmol) in acetophenone (25 mL) was added dropwise to the heated solution over a period of one-half hour. The mixture was then allowed to react at 150°C for an additional eight hours with stirring. The acetophenone was then removed by steam distillation. The remaining residue was extracted into toluene; the toluene extracts were combined and evaporated.

The resulting liquid was added to a solution containing 10% sodium hydroxide (100 mL) and 95% ethanol (20 mL) and the mixture was refluxed for two hours, acidified, and extracted several times with diethyl ether. The combined dried (anhydrous sodium sulfate) ether extracts were evaporated. The resulting solid was recrystallized from 40% methanol in water to yield 9.2 g (71%) of a yellow-white solid (3): m.p. 116–118°C; ¹H-NMR (DMSO-*d*₂) δ 5.29 (s, 2, ArCH₂O), 7.26–8.09 (m, 8, aryl-H), and 13.06 (s, 1, COOH); ¹³C-NMR (DMSO-*d*₂) ppm 69.1 (t, ArCH₂O), 111.2 (d, C₂'), 117.1 (d, C₆'), 118.8 (d, C₄'), 128.2, 128.5, 128.6, 130.4, 130.9, 131.7 (aryl-C), 136.8 (s, C₃), 158.2 (s, C₁'), and 166.8 (s, COOH); MS *m/z* (rel. intensity) 296 (12, M⁺), 135 (100), 89 (7), and 77 (8).

3-(α -Hydroxymethyl)benzoic Acid (4). The method of Gilman¹⁰ yielded 0.53 g (8%) of the desired product as a yellow-white solid: m.p. 108–110°C (lit.^{10,11} 111°C, 114.5–115°C); IR (mull) cm⁻¹ 3750 (OH), 1680 (C=O), and 1590 (aryl); ¹H-NMR (DMSO-*d*₂) δ 4.59 (s, 2, ArCH₂-OH), 5.33 (br s, 1, OH), 7.36–7.96 (m, 4,

aryl-H), and 12.89 (br s, 1, COOH); ^{13}C -NMR (DMSO- d_2) ppm 62.9 (t, ArCH $_2$ -OH), 126.9, 127.3, 127.9, 130.3, 130.4 (aryl-C), 142.6 (s, C $_3$), and 167.0 (s, COOH); MS m/z (rel. intensity) 152 (72, M $^+$), 135 (12), 123 (60), 107 (67), 105 (51), 89 (18), 79 (100), and 77 (100).

This compound was also prepared by refluxing a mixture containing methyl α -bromo-3-toluate (4.0 g), concentrated sulfuric acid (6 mL) and water (100 mL) for four hours. The solution was made basic with 10% sodium hydroxide and extracted with diethyl ether to remove any starting material. The aqueous layer was acidified, extracted into diethyl ether, dried, and evaporated to yield a solid. The solid was recrystallized from water to yield 1.79 g of a product identical to that described above.

3-(α -Mercaptomethyl)benzoic Acid (5). The method of Folli and Iarossi¹² yielded 3.7 g (85%) of the desired product as a white solid: m.p. 94-97°C (lit.¹² 105-106°C); IR (mull) cm^{-1} 1690 (C=O), and 1580 (aryl); ^1H -NMR (DMSO- d_2) δ 3.81 (s, 2, ArCH $_2$ SH), and 7.34-7.96 (m, 4, aryl-H); ^{13}C -NMR (DMSO- d_2) ppm 27.3 (t, ArCH $_2$ SH), 127.3, 128.2, 128.7, 130.9, 132.1 (aryl-C), 141.7 (s, C $_3$), and 166.9 (s, COOH); MS m/z (rel. intensity) 168 (45, M $^+$), 135 (100), 89 (11), and 77 (18).

10-Hydroxy-10-(3'-carboxybenzyl)-9(10H)-anthracenone (6). The method of Dimmel and Shepard¹³ to synthesize AHQ-adducts was used to prepare anthrahydroquinone and the desired adduct. A sufficient quantity of anthrahydroquinone (10-12 mmol) was prepared under a nitrogen atmosphere and dissolved in a mixture containing 30 mL of water and 7.5 mL of 30% sodium hydroxide solution.

3-(α -Bromomethyl)benzoic acid¹⁴ (2.0 g, 9.3 mmol) was quickly added in solid form to the stirring solution. The solution immediately turned from a red to a tan color; the red color indicates the presence of AHQ ions. Additional sodium hydroxide was added, and the mixture was heated to 55-60°C for 1 hour and then allowed to cool. The mixture was filtered to remove precipitated anthraquinone. The filtrate was acidified, extracted into diethyl ether, dried over anhydrous sodium sulfate, and evaporated to a yellow solid. Recrystallization from 95% ethanol yielded 1.05 g (33%) of 6 as a white solid: m.p. 212-215°C; IR (mull) cm^{-1} 3480 (HO), 1680 (C=O), and 1590 (C=C); ^1H -NMR (DMSO- d_2) δ 3.22 (s, 2, CH $_2$), 6.22 (d of t, J = 1.5 Hz and 7.7 Hz, 1, C $_4$ -H), 6.48 (br s, 0.7, OH), 6.71 (t, J = 1.5 Hz, 1, C $_2$ -H), 6.93 (t, J = 7.7 Hz, 1, C $_5$ -H), 7.38-8.03 (m, 9, other

aryl-H), and 12.47 (br s, 0.7, COOH); ^{13}C -NMR (DMSO- d_2) ppm 54.9 (t, CH_2), 72.4 (s, C_{10}), 125.1, 126.4, 126.8, 127.0, 127.4, 129.4, 130.3, 130.8, 133.0, 133.9 (aryl-C), 135.1 (s, C_3), 147.1 (s, C_{4a} , C_{5a}), 166.5 (s, COOH), and 181.6 (s, C_9); MS m/z (rel. intensity) 344 (M^+ , 0.2), 209 (100), 152 (14). Assignment of NMR chemical shifts were aided by assignments given in Ref. 13.

3-(3'-Carboxybenzylthiomethyl)benzoic Acid (10). 3-(α -Bromomethyl)benzoic acid (2.0 g, 9.30 mmol) and 3-(α -mercaptomethyl)benzoic acid (1.6 g, 9.45 mmol) were dissolved in 1 M sodium hydroxide (40 mL). The solution was refluxed with stirring for 8 hours, cooled, acidified with 6 M hydrochloric acid, and extracted with diethyl ether. The combined ether extracts were dried and evaporated to yield a solid, which was recrystallized from 95% ethanol to yield 1.8 g (49%) of the 10 as a yellow-white solid: m.p. 197-198°C (lit.¹⁵ 197°C); IR (mull) cm^{-1} 1685 (C=O-), and 1610 (C=C); ^1H -NMR (DMSO- d_2) δ 3.77 (s, 4, CH_2), 7.35-7.90 (m, 8, aryl-H), and 12.94 (br s, 1.3, COOH); ^{13}C -NMR (DMSO- d_2) ppm 34.8 (t, CH_2), 127.5, 128.2, 129.3, 130.6, 132.8 (aryl-C), 138.4 (s, C_3), and 166.7 (s, COOH); MS m/z (rel. intensity) 302 (M^+ , 11), 167 (23), 135 (100), 121 (9), 89 (15), 77 (25), and 45 (12).

High Temperature Reactions of 3 and Product Analysis. The same "bomb" and reaction sample workup procedures as those used for the *cis*-cinnamic acid isomerization study³ were employed here. The only differences were that two internal standards were employed here, the sample was split, and analyses for carboxylic acids (as methyl esters)³ and for phenols (as benzoates)¹⁶ were performed separately. The temperature program used for the analysis of the carboxylic acid methyl esters was 130°C for 1 minute, 10°C min⁻¹ to 250°C, 30°C min⁻¹ to 300°C, and held at 300°C. The retention times were: methyl 3-toluate, 2.2 min; methyl 3-hydroxybenzoate 4.9 min; methyl 3-(α -hydroxymethyl)benzoate, 6.3 min; dimethyl isophthate, 6.3 min; methyl 3-(α -mercaptomethyl)benzoate, 6.7 min; methyl 3-[3'-(α,α,α -trifluoromethyl)phenoxyethyl]benzoate, 10.9 min; methyl 4-benzyloxybenzoate (internal standard), 12.4 min; methyl 3-(3'-carboxybenzylthiomethyl)benzoate, 16.8 min; 10-hydroxy-10-(3'-carboxybenzyl)-9(10H)-anthracenone, 22.2 min. The temperature program for analysis of benzoylated phenols was the same as above except the initial column temperature was 160°C. The retention times (as benzoates) were: 3-trifluoromethylphenol, 3.6 min; 4-isopropylphenol (internal standard), 7.3 min.

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